$$\mathrm{Fe}(\eta^2\text{-}\mathrm{Ph_2PCH{=}C}(t\text{-}\mathrm{Bu})\mathrm{S})(\eta^2\text{-}\mathrm{SCOMe})(\mathrm{PPh_3})(\mathrm{CO}) + \mathrm{HCl} + \mathrm{H_2O} \rightarrow \mathrm{ClFe}(\eta^2\text{-}\mathrm{Ph_2PCH{=}C}(t\text{-}\mathrm{Bu})\mathrm{S})(\mathrm{PPh_3})(\mathrm{CO})_2 + \mathrm{H_2S} + \mathrm{MeOH}$$

Although there was no direct evidence for this, it seems probable that the formation of **7** results from the hydrolysis of **5**, following the sequence **1** → **2** → **5** → **7**.

Conclusions

The results that are reported here show that the chelating $Ph_2PCH{=}C(R)S^-$ ligand is a reversible proton acceptor and that its neutral iron complexes **1** and **8** behave as weak bases. The protonation of the $Ph_2PCH{=}C(R)S$ chelating ligand of $Fe(\eta^2\text{-}SCOMe)$ complexes **1** promotes the coordination of a halide anion to iron via displacement of its sulfur atom to give the unstable complex **4** or via interconversion of the heteroallene coordination mode from η^2 to η^1, leading finally to a novel tripodal ligand containing iron complex **5**. The iron–chloro derivative **7** can be considered as resulting from the hydrolysis of this tripodal ligand, with regeneration of the initial $Ph_2PCH{=}C(t\text{-}Bu)S^-$ chelating ligand. The protonation appears as a competitive but reversible pathway in the transformation of the $Fe(\eta^1\text{-}C(OMe)S)$ complexes **8** into the thiocarbonyliron derivatives **10** and **11**. Finally, the readily available $Ph_2PCH{=}C(t\text{-}Bu)S$ chloro–iron derivative **7** appears particularly attractive for conversion to other $Ph_2PCH{=}C(t\text{-}Bu)S$ iron derivatives.

Acknowledgment. This work was supported by CNRS and the "Progetto bilaterale" approved by Italian CNR. Thanks are due to Dante Masi for technical assistance during the X-ray work.

Registry No. **1a**, 82264-89-9; **1b**, 82247-29-8; **2a**, 110614-72-7; **2b**, 110614-75-0; **3a**, 110614-73-8; **3b**, 110614-76-1; **4**, 110614-77-2; **5**, 110614-78-3; **6**, 110637-29-1; **7**, 92543-95-8; **8a**, 92543-92-5; **8b**, 110614-79-4; **10**, 110614-81-8; **11a**, 110614-83-0; **11b**, 110614-82-9; $Ph_2PC{\equiv}C\text{-}t\text{-}Bu$, 33730-51-7; $Ph_2PC{\equiv}CPh$, 7608-17-5; PPh_2Cl, 1079-66-9; $(PPh_3)_2(CO)_2(CS_2)Fe$, 86196-40-9; *tert*-butylacetylene, 917-92-0; phenylacetylene, 536-74-3.

Supplementary Material Available: Tables of anisotropic thermal parameters and positional parameters of hydrogen atoms (4 pages); listings of structure factors (20 pages). Ordering information is given on any current masthead page.

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(19) The evolved H_2S was quantitatively determined by precipitation as ZnS or HgS. The formation of **7** has been found to be slow as compared to those of **5** under similar acidic conditions, and it could be assumed that **7** arises from the hydrolysis of **5**. When $CHCl_3$ was used instead of CH_2Cl_2 for the preparation of **7**, an orange crystalline product resulted which showed in the solid state two IR carbonyl frequencies (2013, 1962 cm^{-1}) different from those (2025, 1975 cm^{-1}) showed by the product obtained from CH_2Cl_2 conditions. The same ^1H and ^{31}P NMR and IR spectra were found in solution [IR (cyclohexane solution) 2025, 1977 cm^{-1}]. Analysis shows that from $CHCl_3$, **7** crystallized as $7\cdot CHCl_3$. Anal. Found (Calcd) C, 56.61 (56.54); H, 4.44 (4.38); P, 6.79 (7.48); S, 2.83 (3.87); Cl, 17.25 (17.12).

Synthesis and Complexation of a New Chelating Bis(phosphite) Ligand, pinacop. Structural Characterization of (2,4-Dimethylpentadienyl)M(pinacop) Complexes (M = Co, Rh)[1]

John R. Bleeke,* Andrew J. Donaldson, and Wei-Jun Peng

Department of Chemistry, Washington University, St. Louis, Missouri 63130

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A new chelating bis(phosphite) ligand, $\overline{\mathrm{OCMe_2CMe_2OP}}\mathrm{OCMe_2CMe_2O}\overline{\mathrm{POCMe_2CMe_2O}}$ or "pinacop", has been synthesized via condensation of pinacol with phosphorus trichloride. The addition of pinacop to the low-temperature reaction product of $CoCl_2$ and 2 equiv of potassium 2,4-dimethylpentadienide yields (2,4-dimethylpentadienyl)Co(pinacop) (**1**), which has been structurally characterized. **1** crystallizes in the monoclinic space group *Cc* with $a = 13.964$ (7) Å, $b = 16.018$ (5) Å, $c = 13.775$ (3) Å, $\beta = 108.58$ (3)°, $V = 2921$ (2) Å^3, and $Z = 4$. The pinacop ligand is oriented with one phosphorus atom eclipsing the open edge and the other phosphorus atom eclipsing the central carbon, C3, of the U-shaped η^5-dimethylpentadienyl group. (2,4-Dimethylpentadienyl)Rh(pinacop) (**2**) has been synthesized by reacting $[(\text{pinacop})RhCl]_2$ with 2 equiv of potassium 2,4-dimethylpentadienide and has been structurally characterized. **2** crystallizes in the monoclinic space group $P2_1/n$ with $a = 10.609$ (3) Å, $b = 25.241$ (6) Å, $c = 11.500$ (1) Å, $\beta = 104.36$ (2)°, $V = 2983$ (1) Å^3, and $Z = 4$. The dimethylpentadienyl ligand in **2** is bonded to the Rh center in an η^3 fashion and adopts an anti-rotated (sickle shaped) geometry. The overall coordination geometry for 16 e^- **2** is square planar with C1 and C3 of the dimethylpentadienyl ligand and P1 and P2 of the pinacop ligand occupying the four coordination sites. In solution, **2** exists as an equilibrium mixture of *anti*-η^3- and *syn*-η^3-2,4-dimethylpentadienyl isomers. The anti isomer undergoes a fluxional process, which exchanges the ends of the dimethylpentadienyl ligand via an 18 e^- (η^5-2,4-dimethylpentadienyl)Rh(pinacop) intermediate.

Introduction

Chelating ligands can dramatically influence the reactivity of transition-metal complexes.[2] For this reason, considerable effort has been directed toward synthesizing metal complexes containing chelating poly(tertiary phosphine) ligands.[2,3] In contrast, there have been no reports

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[1] Pentadienyl-Metal-Phosphine Chemistry. 13. For the previous paper in this series, see Bleeke, J. R.; Peng, W.-J. *Organometallics* **1987**, *6*, 1576.

(2) Pignolet, L. H. *Homogeneous Catalysis with Metal Phosphine Complexes*; Plenum: New York, 1983.

(3) McAuliffe, C. A.; Levason, W. *Phosphine, Arsine, and Stibine Complexes of the Transition Elements*; Elsevier: Amsterdam, 1979.

0276-7333/88/2307-0033$01.50/0

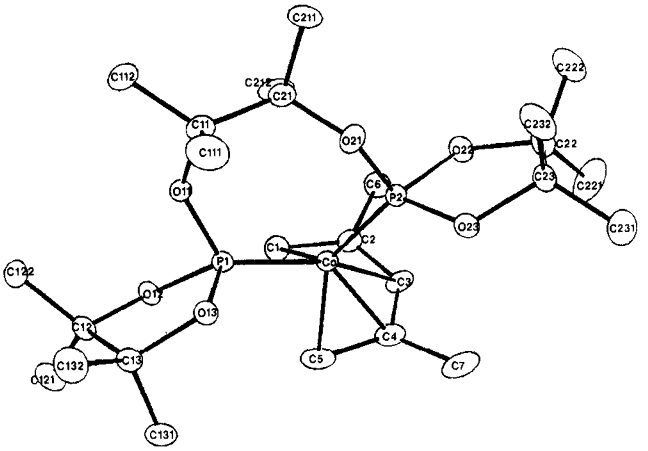

Figure 1. ORTEP drawing of (η^5-2,4-dimethylpentadienyl)Co(pinacop), 1. Hydrogen atoms are omitted for clarity.

to date of transition-metal complexes containing chelating poly(tertiary *phosphite*) ligands.[4] The weaker σ-donor and stronger π-acceptor properties of these ligands, as compared to poly(tertiary phosphines),[5] should impart to metal centers substantially different electronic environments and reactivities.

In order to begin to probe the chemistry of chelating phosphite ligands, we have developed a straightforward, inexpensive synthesis of a new, crystalline bis(phosphite) compound, $OCMe_2CMe_2OPOCMe_2CMe_2OPOCMe_2CMe_2O$ ("pinacop" for pinacol plus phosphorus trichloride).[6] This ligand has been coordinated to (dimethylpentadienyl)Co and (dimethylpentadienyl)Rh moieties and the structures of the resulting compounds, (η^5-2,4-dimethylpentadienyl)Co(pinacop) (**1**) and (η^3-2,4-dimethylpentadienyl)Rh(pinacop) (**2**), have been determined by X-ray diffraction techniques. Significantly, **2** is the first example of a solid, crystalline (pentadienyl)-RhP_2 complex. The monodentate phosphine analogues, (η^3-2,4-dimethylpentadienyl)RhP_2 [P = PMe_3, PEt_3, P(*i*-Pr)$_3$, P(*i*-Bu)$_3$], are all oils or low-melting solids and are not, therefore, amenable to X-ray structural studies.[7]

Results and Discussion

The chelating bis(phosphite), $OCMe_2CMe_2OPOCMe_2CMe_2OPOCMe_2CMe_2O$ (pinacop), is produced in good yield from the reaction of 3 mol of pinacol ($HOCMe_2CMe_2OH$) with 2 mol of PCl_3 in the presence of 6 mol of *N*,*N*-dimethylaniline and can be crystallized as a white solid from pentane. Pinacop exhibits three ^1H NMR signals of equal intensity, which are due to the three types of methyl groups—bridge methyls, ring methyls endo to the bridge, and ring methyls exo to the bridge. The $^{13}C\{^1H\}$ NMR spectrum consists of three methyl signals and two quaternary carbon signals (bridge and ring), while the $^{31}P\{^1H\}$ NMR spectrum is a singlet 1 ppm downfield from $P(OMe)_3$.

Table I. Positional Parameters with Estimated Standard Deviations for Non-Hydrogen Atoms in (η^5-2,4-Dimethylpentadienyl)Co(pinacop), 1[a]

atom	*x*	*y*	*z*	*B*, Å^2
Co	0.000	−0.12565 (5)	0.000	3.56 (1)
P1	−0.1112 (1)	−0.03650 (9)	−0.0118 (1)	3.25 (3)
P2	0.1275 (1)	−0.0498 (1)	0.0647 (1)	3.57 (3)
O11	−0.1053 (3)	0.0517 (3)	−0.0633 (3)	3.94 (9)
O12	−0.2260 (3)	−0.0617 (3)	−0.0808 (3)	4.06 (9)
O13	−0.1452 (3)	−0.0121 (3)	0.0854 (3)	4.03 (9)
O21	0.1164 (4)	0.0497 (3)	0.0520 (4)	5.4 (1)
O22	0.2346 (3)	−0.0668 (4)	0.0427 (3)	5.3 (1)
O23	0.1825 (3)	−0.0519 (3)	0.1859 (3)	4.6 (1)
C1	−0.0652 (5)	−0.1731 (5)	−0.1483 (6)	5.5 (2)
C2	0.0337 (6)	−0.2047 (4)	−0.1037 (5)	4.9 (2)
C3	0.0685 (6)	−0.2388 (4)	−0.0041 (5)	5.2 (2)
C4	0.0201 (6)	−0.2404 (4)	0.0715 (5)	5.4 (2)
C5	−0.0835 (6)	−0.2191 (4)	0.0464 (7)	6.9 (2)
C6	0.1130 (6)	−0.1899 (5)	−0.1561 (5)	6.1 (2)
C7	0.0851 (7)	−0.2595 (5)	0.1788 (6)	8.0 (2)
C11	−0.0351 (5)	0.1226 (4)	−0.0363 (5)	5.0 (2)
C12	−0.3060 (4)	−0.0239 (4)	−0.0470 (5)	4.1 (1)
C13	−0.2544 (5)	−0.0162 (4)	0.0699 (5)	4.6 (1)
C21	0.0686 (5)	0.0965 (5)	−0.0397 (6)	5.2 (2)
C22	0.3271 (5)	−0.0645 (6)	0.1287 (6)	5.7 (2)
C23	0.2922 (5)	−0.0339 (6)	0.2183 (5)	5.0 (2)
C111	−0.0314 (7)	0.1542 (6)	0.0676 (6)	7.4 (2)
C112	−0.0843 (6)	0.1877 (5)	−0.1173 (7)	7.4 (2)
C121	−0.3955 (5)	−0.0810 (6)	−0.0810 (7)	6.5 (2)
C122	−0.3345 (5)	0.0606 (5)	−0.1014 (5)	5.3 (2)
C131	−0.2731 (6)	−0.0926 (5)	0.1255 (6)	6.5 (2)
C132	−0.2867 (6)	0.0601 (5)	0.1150 (6)	6.9 (2)
C211	0.1426 (6)	0.1717 (5)	−0.0298 (7)	7.0 (2)
C212	0.0616 (6)	0.0479 (5)	−0.1381 (5)	6.4 (2)
C221	0.3647 (8)	−0.1554 (7)	0.1429 (8)	11.5 (3)
C222	0.4033 (6)	−0.0082 (8)	0.1033 (7)	10.6 (4)
C231	0.3385 (7)	−0.0810 (8)	0.3153 (7)	8.6 (3)
C232	0.3065 (6)	0.0600 (6)	0.2389 (8)	7.7 (3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

The reaction of $CoCl_2$ with 2 equiv of potassium 2,4-dimethylpentadienide[8] at −78 °C, followed by addition of pinacop and warming to room temperature, produces (η^5-2,4-dimethylpentadienyl)Co(pinacop).[9] An ORTEP drawing of 1, derived from a single crystal X-ray diffraction study, is shown in Figure 1. Atomic coordinates for the non-hydrogen atoms are listed in Table I; important bond distances and bond angles are reported in Table II. In the solid state, the pinacop ligand is oriented with its two ends in different chemical environments—P1 under the open mouth of the η^5-2,4-dimethylpentadienyl ligand and P2 under its central carbon atom, C3. This inequivalence of the two ends of the bis(phosphite) ligand is retained in solution and gives rise to a doubling in the number of pinacop NMR signals as compared to the free ligand. Hence, the ^1H NMR spectrum contains six pinacop methyl signals, the $^{13}C\{^1H\}$ NMR spectrum includes six pinacop methyl signals (not all distinguishable) and four quaternary carbon signals, and the $^{31}P\{^1H\}$ NMR spectrum contains

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(4) Several reports of complexes containing chelating dialkyl phosphonite ligands such as $(MeO)_2PCH_2CH_2P(OMe)_2$ have appeared. (a) King, R. B.; Rhee, W. M. *Inorg. Chem.* **1978**, *17*, 2961. (b) King, R. B.; Bibber, J. W. *Inorg. Chim. Acta* **1982**, *59*, 197. (c) Fryzuk, M. D. *Inorg. Chem.* **1982**, *21*, 2134. (d) Fryzuk, M. D. *Organometallics* **1982**, *1*, 408.

(5) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(6) The synthesis of the unmethylated analogue of 1, $OCH_2CH_2OPOCH_2CH_2OPOCH_2CH_2O$, from the reaction of $HOCH_2CH_2OH$ with 2 equiv of $OCH_2CH_2OPNMe_2$ has been reported. However, the reaction of $HOCMe_2CMe_2OH$ with 2 equiv of $OCMe_2CMe_2OPNMe_2$ failed to produce more than a trace of 1. See Burgada, R.; Germa, H.; Wilson, M.; Mathis, F. *Tetrahedron* **1971**, *27*, 5833.

(7) Bleeke, J. R.; Donaldson, A. J. *Organometallics* **1986**, *5*, 2401.

(8) (a) Yasuda, H.; Ohnuma, Y.; Yamauchi, M.; Tani, H.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2036. (b) When the volatiles were removed by vacuum from a solution of potassium 2,4-dimethylpentadienide in tetrahydrofuran, the composition of the residual solid product was approximately $K^+C_7H_{11}^-\cdot0.7THF$. This value was used for all stoichiometric calculations.

(9) (η^5-2,4-Dimethylpentadienyl)$Co(PR_3)_2$ complexes have been synthesized by a similar approach. (a) Bleeke, J. R.; Peng, W.-J. *Organometallics* **1984**, *3*, 1422. (b) Bleeke, J. R.; Peng, W.-J. *Organometallics* **1986**, *5*, 635.

Table II. Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations for 1 and 2

Bond Distances

	1	2		1	2
M–P1	2.078 (2)	2.186 (1)	C4–C7	1.50 (1)	1.47 (1)
M–P2	2.105 (2)	2.182 (1)	P–O max,	1.640 (5),	1.628 (3),
M–C1	2.096 (8)	2.190 (5)	min,	1.595 (5),	1.609 (3),
M–C2	2.072 (7)	2.153 (5)	av of 6	1.61 (1)	1.619 (7)
M–C3	2.059 (7)	2.252 (5)	O–C max,	1.408 (8),	1.468 (5),
M–C4	2.062 (8)		min,	1.44 (1),	1.450 (6),
M–C5	2.118 (9)		av of 6	1.46 (2)	1.46 (1)
C1–C2	1.41 (1)	1.389 (7)	C–C[a] max,	1.54 (1),	1.550 (6),
C2–C3	1.41 (1)	1.448 (7)	min,	1.52 (1),	1.540 (7),
C2–C6	1.52 (1)	1.507 (7)	av of 3	1.53 (2)	1.54 (1)
C3–C4	1.41 (1)	1.409 (8)			
C4–C5	1.42 (1)	1.369 (8)			

Bond Angles

	1	2		1	2		1	2
P1–M–P2	98.43 (7)	94.99 (4)	O11–P1–O12	98.1 (3)	95.4 (2)	O12–C12–C13	102.4 (5)	103.9 (4)
P1–M–C1	95.2 (2)	96.9 (1)	O11–P1–O13	103.1 (3)	106.1 (2)	O13–C13–C12	105.8 (5)	102.6 (4)
P1–M–C3	161.0 (3)	164.3 (1)	O12–P1–O13	92.8 (2)	94.4 (2)	O21–C21–C11	107.2 (7)	109.3 (4)
P1–M–C5	92.3 (3)		O21–P2–O22	101.9 (4)	100.8 (2)	O22–C22–C23	103.6 (6)	102.9 (3)
P2–M–C1	131.9 (3)	168.0 (1)	O21–P2–O23	97.6 (3)	99.2 (2)	O23–C23–C22	104.9 (6)	104.6 (4)
P2–M–C3	100.5 (3)	99.7 (1)	O22–P2–O23	91.5 (3)	94.5 (2)	C1–C2–C3	123.2 (8)	123.7 (5)
P2–M–C5	138.9 (3)		P1–O11–C11	134.2 (4)	132.9 (3)	C1–C2–C6	119.7 (8)	117.9 (5)
C1–M–C3	73.5 (3)	68.5 (2)	P1–O12–C12	114.6 (4)	112.8 (3)	C3–C2–C6	116.4 (8)	117.6 (5)
C1–M–C5	85.9 (4)		P1–O13–C13	115.8 (4)	113.1 (3)	C2–C3–C4	128.8 (8)	131.1 (6)
C3–M–C5	72.0 (4)		P2–O21–C21	127.9 (5)	132.3 (3)	C3–C4–C5	120.5 (9)	117.9 (7)
M–P–O max,	121.6 (2),	120.5 (1),	P2–O22–C22	118.2 (5)	112.8 (3)	C3–C4–C7	116.7 (9)	122.0 (6)
min,	116.5 (2),	117.2 (1),	P2–O23–C23	114.7 (4)	113.5 (3)	C5–C4–C7	122.7 (8)	120.0 (7)
av of 6	119.6 (5)	119.0 (2)	O11–C11–C21	110.1 (6)	111.7 (3)			

[a] Ring and bridge.

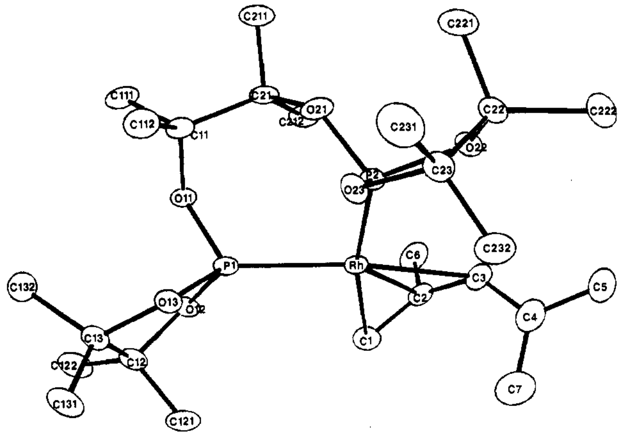
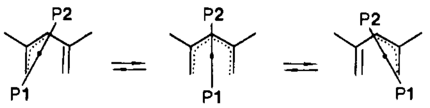


Figure 2. ORTEP drawing of (η^3-2,4-dimethylpentadienyl)Rh(pinacop), **2**. Hydrogen atoms are omitted for clarity.

Scheme I



two signals. The structural and spectroscopic features of the η^5-2,4-dimethylpentadienyl ligand are very similar to those which we reported earlier for (η^5-2,4-dimethylpentadienyl)Co(PEt$_3$)$_2$.[9a]

The reaction of [(pinacop)RhCl]$_2$ with 2 equiv of potassium 2,4-dimethylpentadienide[8] at −78 °C followed by warming to room temperature yields yellow (η^3-2,4-dimethylpentadienyl)Rh(pinacop) (**2**).[10] Compound **2**, unlike its monodentate phosphine analogues, (η^3-2,4-dimethylpentadienyl)RhP$_2$ [P = PMe$_3$, PEt$_3$, P(i-Pr)$_3$, and P(i-Bu)$_3$],[7] is a crystalline solid at room temperature and has been structurally characterized by X-ray diffraction. An ORTEP drawing of the structure is presented in Figure 2. Atomic coordinates are listed in Table III, while bond distances and angles are given in Table II. The overall coordination geometry of **2** is square planar with C1 and C3 of the η^3-2,4-dimethylpentadienyl ligand and P1 and P2 of the pinacop ligand occupying the four coordination sites.

The η^3-dimethylpentadienyl ligand adopts an anti-rotated (sickle-shaped) geometry in the solid state (see drawing).

As in other structures of (*anti*-η^3-pentadienyl)M complexes,[11] the vinylic moiety (C3/C4/C5) is bent substantially out of the plane of the allylic moiety (C1/C2/C3) away from the metal atom; these two planes intersect at a dihedral angle of 36.6°. This deformation is electronically advantageous because it points the p orbital on C3 more directly at the metal center and is sterically favorable because it moves the vinylic moiety away from the metal and its ligands. On the other hand, there is very little rotation about C3–C4. Hence, torsional angle C2–C3–C4–C5 is 164.0° and atoms C2/C3/C4/C5 are coplanar to within 0.1 Å. Perhaps the most surprising structural feature of the η^3-dimethylpentadienyl ligand is the shortness of the bond between C3 and C4 (1.409 Å). This short bond distance suggests that despite the coordination of rhodium to an allylic moiety, the η^3-dimethylpentadienyl ligand still retains substantial π-electron delocalization.

When crystalline **2** is dissolved in acetone, an equilibrium mixture of the anti-η^3 and syn-η^3 isomers in an ap-

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[10] (η^3-2,4-Dimethylpentadienyl)Rh(PR$_3$)$_2$ complexes have been synthesized by a similar approach. See ref 7.

[11] For structural reports of (*anti*-η^3-pentadienyl)metal complexes, see ref 9a and Paz-Sandoval, M. A.; Powell, P. *Organometallics* **1984**, *3*, 1470.

Table III. Positional Parameters wth Estimated Standard Deviations for Non-Hydrogen Atoms in (η^3-2,4-Dimethylpentadienyl)Rh(pinacop), 2[a]

atom	x	y	z	B, Å^2
Rh	0.21156 (3)	0.11214 (1)	0.26201 (3)	2.906 (5)
P1	0.2514 (1)	0.02740 (5)	0.25462 (9)	2.81 (2)
P2	0.3544 (1)	0.13623 (4)	0.1646 (1)	3.03 (2)
O11	0.3990 (3)	0.0083 (1)	0.3090 (2)	3.10 (6)
O12	0.1877 (3)	−0.0129 (1)	0.3348 (3)	3.60 (6)
O13	0.1989 (3)	−0.0055 (1)	0.1308 (2)	3.25 (6)
O21	0.4994 (3)	0.1126 (1)	0.2071 (3)	4.46 (7)
O22	0.3851 (3)	0.1985 (1)	0.1528 (3)	3.52 (6)
O23	0.3268 (3)	0.1247 (1)	0.0215 (3)	3.73 (7)
C1	0.0583 (5)	0.1056 (2)	0.3585 (5)	4.8 (1)
C2	0.1313 (4)	0.1511 (2)	0.3939 (4)	4.1 (1)
C3	0.1483 (5)	0.1924 (2)	0.3116 (5)	4.7 (1)
C4	0.0581 (6)	0.2176 (2)	0.2172 (5)	5.9 (1)
C5	0.0947 (7)	0.2641 (2)	0.1737 (7)	7.2 (2)
C6	0.2152 (6)	0.1535 (3)	0.5204 (5)	6.2 (1)
C7	−0.0725 (8)	0.1956 (3)	0.1658 (8)	8.7 (2)
C11	0.5223 (4)	0.0209 (2)	0.2789 (4)	3.34 (9)
C12	0.1002 (5)	−0.0519 (2)	0.2619 (4)	4.0 (1)
C13	0.1549 (5)	−0.0590 (2)	0.1501 (4)	4.0 (1)
C21	0.5625 (4)	0.0795 (2)	0.3077 (4)	3.64 (9)
C22	0.4154 (4)	0.2116 (2)	0.0383 (4)	3.58 (9)
C23	0.3302 (5)	0.1723 (2)	−0.0499 (4)	3.8 (1)
C111	0.6157 (5)	−0.0171 (2)	0.3623 (5)	4.7 (1)
C112	0.5139 (5)	0.0077 (2)	0.1487 (4)	5.1 (1)
C121	−0.0358 (5)	−0.0284 (2)	0.2343 (6)	5.5 (1)
C122	0.1060 (6)	−0.1014 (2)	0.3375 (5)	5.7 (1)
C131	0.0535 (6)	−0.0743 (2)	0.0364 (5)	5.5 (1)
C132	0.2713 (6)	−0.0962 (2)	0.1686 (6)	5.5 (1)
C211	0.7067 (5)	0.0876 (3)	0.3127 (6)	5.7 (1)
C212	0.5338 (5)	0.0992 (2)	0.4228 (5)	4.5 (1)
C221	0.5618 (5)	0.2032 (2)	0.0523 (5)	5.2 (1)
C222	0.3816 (6)	0.2691 (2)	0.0130 (6)	5.7 (1)
C231	0.3831 (6)	0.1557 (3)	−0.1553 (5)	6.2 (1)
C232	0.1890 (6)	0.1910 (2)	−0.0913 (6)	6.2 (2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

proximate ratio of 4:1 is rapidly produced.[12] The anti isomer (**2a**) is fluxional at room temperature while the syn isomer (**2s**) is static. The dynamic process exhibited by **2a** exchanges the ends of the 2,4-dimethylpentadienyl ligand. Hence, in the ^{13}C NMR spectrum at 20 °C, C1 is equivalent to C5, C2 is equivalent to C4, and C6 is equivalent to C7. Similarly, in the ^{1}H NMR spectrum at 20 °C, H1$_{\text{inner}}$ is equivalent to H5$_{\text{inner}}$, H1$_{\text{outer}}$ is equivalent to H5$_{\text{outer}}$, and the pentadienyl methyl groups are equivalent. Consistent with these observations is the "windshield wiper" fluxional process shown in Scheme I, which we proposed earlier to explain the dynamic behavior exhibited by (*anti*-η^3-2,4-dimethylpentadienyl)RhP$_2$ (P = monodentate phosphine) complexes.[7] The barrier for this fluxional process, ΔG^*, estimated from line-shape simulations of the variable temperature (−80 → 20 °C) NMR spectra, is 8.0 ± 0.5 kcal.[13]

The NMR spectra of the pinacop ligand in **2a** (the anti isomer) at room temperature are similar to those observed for **1**, because the end-to-end fluxional process produces mirror-plane symmetry. In **2s** (the syn isomer), on the other hand, there is no mirror plane, so each carbon of the dimethylpentadienyl ligand and each carbon of the pinacop ligand is unique.

Experimental Section

A. General Procedures. All manipulations were carried out under an inert atmosphere, using either drybox or Schlenk techniques. Tetrahydrofuran and diethyl ether were dried with sodium/benzophenone and distilled before use. Pentane was dried over calcium hydride and distilled. Pinacol (Aldrich), PCl$_3$ (Aldrich), *N*,*N*-dimethylaniline (Aldrich), and CoCl$_2$ (Alfa) were used without further purification. [(*cis*-Cyclooctene)$_2$RhCl]$_2$[14] and potassium 2,4-dimethylpentadienide–tetrahydrofuran[8] were prepared by following literature procedures. NMR experiments were performed on a Varian XL-300 NMR spectrometer. ^{1}H (300 MHz) and ^{13}C (75 MHz) spectra were referenced to tetramethylsilane, while ^{31}P (121 MHz) spectra were referenced to H$_3$PO$_4$. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

B. Synthesis of $\mathrm{OCMe_2CMe_2OPOCMe_2CMe_2O\text{-}POCMe_2CMe_2O}$, pinacop. Pinacol (HOCMe$_2$CMe$_2$OH, 17.7 g, 0.15 mol), *N*,*N*-dimethylaniline (36.3 g, 0.30 mol), and 250 mL of diethyl ether were placed in a 500-mL three-necked flask, which was fitted with a condenser, a mechanical stirrer, and an addition funnel containing PCl$_3$ (13.7 g, 0.10 mol) in 50 mL of diethyl ether. The pinacol solution was cooled to 0 °C and the PCl$_3$ was added dropwise with stirring. The reaction mixture was stirred for 12 h, filtered to remove the white solid (C$_6$H$_5$NMe$_2$H$^+$Cl$^-$), and evaporated to dryness. The product was extracted with pentane and crystallized from pentane at −30 °C; yield of crystalline product, 9.0 g (44%). ^{31}P{^{1}H} NMR (20 °C, benzene-d_6, referenced to H$_3$PO$_4$): δ 141.9 (s). ^{1}H NMR (20 °C, toluene-d_8): δ 1.54, 1.31, 1.11 (br s's, 1:1:1, ring Me's endo to bridge, ring Me's exo to bridge, bridge Me's). ^{31}C{^{1}H} NMR (20 °C, toluene-d_8): δ 84.1 (d, $J_{\text{C-P}}$ = 7 Hz, ring quaternary C's), 81.5 (d, $J_{\text{C-P}}$ = 7 Hz, bridge quaternary C's), 25.8, 25.5, 25.3 (s's, methyl C's). Anal. Calcd for P$_2$O$_6$C$_{18}$H$_{36}$: C, 52.67; H, 8.86. Found: C, 52.68; H, 8.58.

C. Synthesis of (η^5-2,4-Dimethylpentadienyl)Co(pinacop) (1). CoCl$_2$ (1.29 g, 0.010 mol) was stirred in 100 mL of tetrahydrofuran for 12 h to form a blue solution with some undissolved CoCl$_2$. This solution was cooled to −78 °C, and potassium 2,4-dimethylpentadienide–0.7-tetrahydrofuran[8b] (3.70 g, 0.020 mol) in 50 mL of tetrahydrofuran was added dropwise with stirring, producing a dark green solution, which was stirred for an additional 0.5 h at −78 °C. The chelating bis(phosphite) ligand, pinacop (4.10 g, 0.010 mol), in 20 mL of tetrahydrofuran was added dropwise and then the solution was slowly warmed to room temperature. Solvent was removed from the resulting dark red solution, and the product, **1**, was extracted from the residue with pentane. **1** crystallized from a saturated pentane solution at −30 °C as red blocks; yield of crystalline product, 1.8 g (32%). ^{31}P{^{1}H} NMR (20 °C, benzene-d_6, referenced to H$_3$PO$_4$): δ 184.9, 153.9 (br s's). ^{1}H NMR (20 °C, toluene-d_8): δ 4.40 (br d, 1, $J_{\text{H-P}}$ = 10.4 Hz, H3), 3.54 (br s, 2, H1$_{\text{outer}}$/H5$_{\text{outer}}$), 2.21 (br s, 6, pentadienyl Me H's), 1.50, 1.49, 1.32, 1.25, 1.14, 1.11 (br s's, 36, phosphite Me H's), 0.89 (br t, 2, $J_{\text{H-P}}$ = 10.4 Hz, H1$_{\text{inner}}$/H5$_{\text{inner}}$). ^{13}C{^{1}H} NMR (20 °C, toluene-d_8): δ 103.3 (s, C2/C4), 91.4 (s, C3), 87.1, 84.8, 83.5, 83.2 (d's, $J_{\text{C-P}}$ = 8 Hz, 1:2:1:2, phosphite quaternary C's), 61.9 (br s, C1/C5), 27–26 (multiplets, pentadienyl and phosphite Me C's). Anal. Calcd for C$_{25}$H$_{47}$CoO$_6$P$_2$: C, 53.18; H, 8.41. Found: C, 52.92; H, 8.55.

D. Synthesis of (η^3-2,4-Dimethylpentadienyl)Rh(pinacop) (2). Pinacop (0.23 g, 5.6 × 10^{-4} mol) was added with swirling to a freshly prepared solution of [(*cis*-cyclooctene)$_2$RhCl]$_2$ (0.20 g, 2.8 × 10^{-4} mol) in 25 mL of tetrahydrofuran. The volatiles were removed under vacuum yielding yellow [(pinacop)RhCl]$_2$ (0.31 g, 2.8 × 10^{-4} mol). This yellow solid was redissolved in tetrahydrofuran and cooled to −78 °C. A solution of potassium 2,4-dimethylpentadienide–0.7-tetrahydrofuran[8b] (0.10 g, 5.6 × 10^{-4} mol) in tetrahydrofuran was added dropwise with stirring. The resulting solution was warmed to room temperature and evaporated to dryness. The product, **2**, was extracted with pentane and crystallized from a saturated pentane solution at −30 °C; yield of **2** (translucent yellow crystals), 0.21 g (62%). The NMR spectra of **2** indicated a 4:1 ratio of anti-η^3 to syn-η^3 isomers. anti-Isomer, **2a**. ^{31}P{^{1}H} NMR (−50 °C,[15] acetone-d_6, referenced to H$_3$PO$_4$): δ 154.2 (d of d, $J_{\text{P-Rh}}$ = 209.6 Hz, $J_{\text{P-P}}$ = 86.6 Hz), 151.7 (d of d, $J_{\text{P-Rh}}$ = 215.6 Hz, $J_{\text{P-P}}$ = 86.6 Hz). ^{1}H NMR (20 °C, acetone-d_6,

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(12) Similar equilibrium mixtures of isomers are observed in (η^3-2,4-dimethylpentadienyl)Rh(PR$_3$)$_2$ systems. See ref 7.

(13) See ref 7 for a more detailed discussion of this calculation.

(14) Van der Ent, A.; Onderdelinden, O. *Inorg. Synth.* **1973**, *14*, 97.

(15) The same spectrum is obtained at 20 °C, but the couplings are less distinct.

Table IV. Crystal and Diffraction Data for 1 and 2

	1	2
formula	$C_{25}H_{47}CoO_6P_2$	$C_{25}H_{47}RhO_6P_2$
mol. wt	564.59	608.57
space group	*Cc*	$P2_1/n$
a, Å	13.964 (7)	10.609 (3)
b, Å	16.018 (5)	25.241 (6)
c, Å	13.775 (3)	11.500 (1)
β, deg	108.58 (3)	104.36 (2)
V, Å^3	2921 (2)	2983 (1)
Z	4	4
crystal color	red	yellow
crystal dimens, mm	0.5 × 0.3 × 0.3	0.5 × 0.4 × 0.2
d_{calcd}, g/cm^3	1.28	1.36
radiation, Å	Mo Kα, $\lambda = 0.71069$	Mo Kα, $\lambda = 0.71069$
scan type	ω	ω
scan rate, deg/min	variable, 4–30	variable, 3–29
scan width, deg	0.6	0.6
2*θ* scan range, deg	3.0–55.0	3.0–55.0
octants collected	$h,k,\pm l$	$h,k,\pm l$
no. unique reflcns measd	3340	6584
no. reflcns w/ $I > 3\sigma(I)$	2198	4297
weighting scheme	non-Poisson contribution, $\rho = 0.80$	non-Poisson contribution, $\rho = 0.80$
decay of stds, %	12.6	0.1
max, min, av decay corr	1.145, 0.999, 1.068	none
μ_{calcd}, cm^{-1}	7.26	7.01
absorp corr	psi scans	psi scans
max, min, av trans factors	0.99, 0.95, 0.97	0.997, 0.851, 0.943
no. of params varied	305	307
data/param ratio	7.2	14.0
R_F[a]	0.044	0.040
R_{wF}[b]	0.048	0.056
goodness-of-fit[c]	1.21	1.11

[a] $R_F = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Goodness-of-fit $= [\sum w(|F_o| - |F_c|)^2/(N_{obsd} - N_{parameters})]^{1/2}$.

fast exchange): δ 4.21 (d, 1, J = 7.5 Hz, H3), 3.63 (s, 2, $H1_{outer}/H5_{outer}$), 3.60 (s, 2, $H1_{inner}/H5_{inner}$), 1.62 (s, 6, pentadienyl Me's), 1.45, 1.42, 1.38, 1.29, 1.27 (overlapping s's, 36, phosphite Me's). $^{13}C\{^1H\}$ NMR (20 °C, acetone-d_6, fast exchange): 131.5 (s, C2/C4), 86.5 (br s, quaternary C's in phosphite bridge), 85.2 (br s, quaternary C's in phosphite rings), 81.3 (t, J = 10.8 Hz, C1/C5), 75.6 (m, C3), 27.5–25.3 (s's, phosphite and pentadienyl Me's). syn-Isomer, **2s**. $^{31}P\{^1H\}$ NMR (−50 °C,[15] acetone-d_6, referenced to H_3PO_4): δ 152.0 (d of d, J_{P-Rh} = 317.4 Hz, J_{P-P} = 87.4 Hz), 148.8 (d of d, J_{P-Rh} = 304.6 Hz, J_{P-P} = 84.3 Hz). ^1H NMR (20 °C, acetone-d_6, stopped exchange): δ 4.78, 4.75 (s's, 2, H5's), 3.38 (d, 1, J = 8.5 Hz, H3), 2.98 (d, 1, J = 5.0 Hz, $H1_{outer}$), 1.96 (s, 3, H6's), 1.75 (s, 3, H7's). Signals due to $H1_{inner}$ and phosphite Me's are obscured. $^{13}C\{^1H\}$ NMR (20 °C, acetone-d_6, stopped exchange): δ 147.2 (d, J = 7.4 Hz, C4), 111.1 (s's, C2, C5), 77.9 (d, J = 37.4 Hz, C3), 57.5 (d of d, J = 34.2 Hz, J = 4.6 Hz, C1). Signals due to C6, C7, and phosphite are obscured. Anal. Calcd for $C_{25}H_{47}RhO_6P_2$: C, 49.34; H, 7.80. Found: C, 49.00; H, 7.55.

E. X-ray Diffraction Studies of 1 and 2. Single crystals of 1 and 2 were sealed in glass capillaries under an inert atmosphere. Data were collected at room temperature on a Nicolet P3 diffractometer with graphite monochromated Mo Kα radiation. All data reduction and refinement were done by using the Enraf-Nonius structure determination package VAX/SDP (modified by B A. Frenz and Assoc., Inc., College Station, TX).[16] Crystal data and details of data collection and structural analysis are summarized in Table IV. Both structures were solved by standard Fourier techniques following the location of the metal atom from a Patterson map. All of the non-hydrogen atoms were refined anisotropically. Hydrogens were added at idealized positions with fixed isotropic thermal parameters (8.0 for H's bonded to C1, C3, and C5 of the dimethylpentadienyl ligands and 10.0 for methyl H's), included in the structure factor calculations, but not refined.

The absolute configuration of 1 was tested by inverting the signs of all the coordinates and performing another refinement. The resulting agreement indices were R_F = 0.045 and R_{wF} = 0.050, higher than those for the configuration reported.

Conclusions

The new chelating bis(phosphite) ligand, $\overline{\mathrm{OCMe_2CMe_2OP}}\mathrm{OCMe_2CMe_2O}\overline{\mathrm{POCMe_2CMe_2O}}$ or "pinacop", has been coordinated to (2,4-dimethylpentadienyl)Co and (2,4-dimethylpentadienyl)Rh moieties. The crystallinity of the rhodium complex has enabled us to determine the solid-state structure of a (pentadienyl)-RhP_2 species for the first time.

We have begun to compare the reactions of the (2,4-dimethylpentadienyl)M[bis(phosphite)] complexes reported herein with those of their bis(phosphine) analogues. We anticipate that the weaker σ-donor and stonger π-acceptor properties of the bis(phosphite) ligand will substantially change the electronic environment at the metal centers and give rise to altered overall reaction chemistries.

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Registry No. 1, 110698-04-9; 2, 110698-05-0; pinacop, 110682-77-4; [(*cis*-cyclooctene)$_2$RhCl]$_2$, 12279-09-3; ((pinacop)-RhCl)$_2$, 110698-06-1; PCl$_3$, 7719-12-2; CoCl$_2$, 7646-79-9; pinacol, 76-09-5; potassium 2,4-dimethylpentadienide, 74205-98-4.

Supplementary Material Available: Listing of final atomic coordinates, thermal parameters, bond lengths, bond angles, significant least-squares planes, and torsional angles for 1 and 2 (19 pages); listings of observed and calculated structure factor amplitudes (26 pages). Ordering information is given on any current masthead page.

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[16] Scattering factors f, f', and f'' were taken from Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Tables 2.2B and 2.3.1.